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(54) IMPROVEMENTS RELATING TO THE AUTOMATIC RINSING OF TABLEWARE OR GLASSES

HOECHST AKTIEN-GESELLSCHAFT, formerly Knapsack Aktiengesellschaft, a body corporate organised under the laws of Germany, of Knapsack bei Koln, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a method of rinsing table-ware or glasses, in an auto-

matic dishwashing machine.

In dishwashing machines, table-ware is subjected to two operations comprising an actual 15 cleaning step and an after-treatment step in a rinsing bath containing a rinse agent or rinse composition, in which the table ware is given a shining surface free from residues. The rinse agents and rinse compositions should have a good wetting power permitting the rinsing water to run off from the table ware so as to remove all residues, e.g. calcium stains or other soilings, therefrom.

The rinse compositions commonly used 25 comprise a blend of different substances, each of which acts in a distinct way, in the rinsing step. More particularly, the rinse composition may contain, for example: an anionic, cationic or non-ionic surfactant as a wetting agent; alcohols as foam inhibitors; an acid ingredient to keep the surface of table-ware free from stains and turbidity caused by lime; and optionally perfume and dyestuffs as further ingredients.

A rinse composition, in which the surfactant is a water-soluble sulphonated condensation product of a phenol, an alkyl phenol or a naphthol and formaldehyde, having a certain molecular weight, has already been disclosed in German published Specification (DOS) No. 1,926,684. Although this is a surfactant producing relatively little foam, the fact remains that it is not to be considered as a non-foaming agent. As a further ingredient, the above 45 known rinse composition may contain an organic carboxylic acid, for example citric acid, tartaric acid or gluconic acid

A disadvantage encountered with certain known rinse compositions is that it is necessary to use a plurality of different chemical substances with the object of obtaining as far as possible a non-foaming rinsing composition producing a satisfactory rinsing effect. Still further, these known rinse compositions are relatively costly.

It is accordingly an object of the present invention to use rinse agents consisting merely of a single chemical compound, which combines in itself all the relevant properties of the known rinse compositions, namely nonfoaming properties together with surface-active and acidic properties. In addition thereto, it should as far as possible be toxicologically unobjectionable, and biologically degradable. Several acid phosphoric acid esters of a certain composition have now been found unexpectedly to satisfy these requirements.

According to the present invention, a method of rinsing table-ware or glasses in an automatic dishwashing machine comprises the use of an aqueous solution or suspension of one or more aliphatic and/or cycloaliphatic phosphoric acid mono- and/or diesters containing from 1 to 4 carbon atoms per alcoholic ester component, or up to 6 in the case of cycloaliphatic ester components, if desired in admixture with phosphoric acid and/or another rinsing agent.

If use is made of the cycloaliphatic esters, they are preferably phosphoric acid mono-and/or di-cyclohexyl esters.

The phosphoric acid esters employed in accordance with the present invention are not restricted to the pure substances or mixtures thereof. Use can also be made of commercialgrade material containing phosphoric acid, for example. In a method in accordance with the present invention it is accordingly also possible to use products comprising aliphatic

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and/or cycloaliphatic phosphoric acid monoesters in admixture with about 5 to 10 weight % of phosphoric acid therein; and further to use mixtures comprising phosphoric acid mono- and diesters in admixture with at most about 5 weight % of phosphoric acid therein.

The phosphoric acid may be used in the form of an aqueous solution with a strength of 75 weight % and added to the other con-10 stituent(s) of the said aqueous solution or suspension, unless it is already present therein as an impurity. The mixture so obtained should preferably contain 50 weight % of phosphoric acid ester and 50 weight % of aqueous phosphoric acid with a strength of 75 weight per cent. The said aqueous solution or suspension is preferably one containing a phosphoric acid ester, if desired in admixture with phosphoric acid, and containing not more than 99 weight % of water.

Still further, it has been discovered that it is possible by the admixture of the present phosphoric acid esters with other rinse composition components to produce rinse compositions more efficient than heretofore. Such a composition may contain between 0 and about 60 weight % of a rinse agent other than the present phosphoric acid esters. A com-

position containing between 0 and 5 weight % of a non-ionic surfactant polycondensation product of iso-

tridecanol and ethylene oxide, 0 and 15 weight % of a non-ionic surfactant polycondensation product of ethylene diamine, ethylene oxide and propylene oxide, 12 and 26 weight % of an aliphatic and/or cycloaliphatic phosphoric acid mono- and/ or di-ester containing from 1 to 4 carbon atoms per alcoholic ester component, or up to 6 in the case of cycloaliphatic ester components, if desired in admixture with phosphoric acid.

0 and 20 weight % of isopropanol, and 45 0 and 20 weight % of citric acid, the balance being, water, perfume and dyestuff, has been found to be particularly useful.

The phosphoric acid esters used in accordance with this invention as rinse agents can be made in known manner, for example by the process reported in German Patent Specification No. 1,226,101. They may be used in a rinsing bath in a concentration substantially between 3 and 300 milligrams/liter, and preferably between 50 and 80 milligrams/liter.

As compared with prior art agents, the rinse agents used in accordance with the present invention, which are based on phosphoric acid esters, have the particular merit of combining in themselves the properties of a surfactant with those of an ingredient of an acidic nature. In addition to this, they are nonfoaming, physiologically harmless and degradable biologically. Heretofore, it has been impossible to combine all these properties in a single substance. Still further, the phosphoric acid esters are commercially readily available and inexpensive.

The following Examples illustrate the in-

vention, without limiting it:

EXAMPLE 1:

A blend of the following composition was prepared and used as a rinse composition in a rinsing bath. The rinse composition was used in the bath in a concentration of 60 milligrams/liter.

3 Weight % of a polycondensation product of 1 mole of isotridecanol with 11 moles of ethylene oxide,

11 weight % of the polycondensation product of ethylene diamine, ethylene oxide and propylene oxide sold as "Genapol PN 30" by Farbwerke Hoechst A.G.,

20 weight % of a blend of phosphoric acid mono- and dimethylesters having a density of 1.56, and

20 weight % of isopropanol, the balance being water.

The rinse composition was visually evaluated as to the formation of foam during the rinsing operation, and also as to the brightdrying effect, viz. as to whether it left any residues on the rinsed articles. Foam could not be found to have been produced. The bright-drying effect was satisfactory.

EXAMPLE 2:

The following rinse composition was

6 Weight % of the above-mentioned poly- 100 condensation product of ethylene diamine, ethylene oxide and propylene oxide,

12 weight % of a blend of phosphoric acid mono- and disopropylesters having a 105 density of 1.4,

20 weight % of citric acid, and 20 weight % of isopropanol, the balance being water.

The rinse composition was used in the 110 rinsing bath at a rate of 36 milligrams/liter, based on the phosphoric acid ester. The rinse composition could not be found to effect the formation of foam. The bright-drying effect was good.

EXAMPLE 3:

The following rinse composition was tested: 11 Weight % of the above-mentioned polycondensation product of ethylene diamine, ethylene oxide and propylene 120 oxide,

23 weight % of a blend of phosphoric acid mono- and diisopropylesters having a density of 1.4, and

20 weight % of citric acid, the balance being water.

The rinse composition was used at the rate

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125

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of 69 milligrams/liter, based on the phos- % of aqueous phosphoric acid with a strength phoric acid ester.

The rinse composition could not be found to effect the formation of foam. The brightdrying effect was very good.

EXAMPLE 4:

The following rinse agent was tested: 20 Weight % of a blend of phosphoric acid mono- and diisopropylesters having a density of 1.4 and 80 weight % of water.

The rinse agent was used at the rate of 60 milligrams/liter, based on the phosphoric acid ester.

Evaluation: Absece of foam formation Brilliant bright-drying effect.

WHAT WE CLAIM IS:

1. A method of rinsing tableware or glasses in an automatic dishwashing machine, comprising the use of an aqueous solution or suspension of one or more aliphatic and/or cycloaliphatic phosphoric acid mono- and/or di-esters containing from 1 to 4 carbon atoms per alcoholic ester component, or up to 6 in the case of cycloaliphatic ester components, if desired in admixture with phosphoric acid and/or another tinsing agent.

2. A method as claimed in claim 1, wherein the phosphoric acid ester is a phosphoric acid mono- and/or dicyclohexyl ester.

3. A method as claimed in either of claims 1 and 2, using one or more aliphatic and/or cycloaliphatic phosphoric acid mono-esters in admixture with about 5 to 10 weight % of phosphoric acid.

4. A method as claimed in either of claims 1 and 2, using one or more phosphoric acid mono- and di-esters in admixture with at most about 5 weight % of phosphoric acid.

5. A method as claimed in any one of claims 1 to 4, using a blend of 50 weight % of one or more phosphoric acid esters and 50 weight of 75 weight %.

6. A method as claimed in any one of claims 1 to 5, using an aqueous solution or suspension of a phosphoric acid ester, if desired in admixture with phosphoric acid, the solution or suspension containing not more than 99 weight % of water.

7. A method as claimed in any one of claims 1 to 6, using between 0 and about 60 weight % of a rinse additive other than those specified in claim 1, as a further ingredient of the aqueous solution or suspension.

8. A method as claimed in claim 1, wherein the aqueous solution or suspension contains between

0 and 5 weight % of a non-ionic surfactant polycondensation product of isotridecanol and ethylene oxide,

0 and 15 weight % of a non-ionic surfactant polycondensation product of ethylene diamine, ethylene oxide and propylene oxide, 12 and 26 weight % of an aliphatic and/or cyclaliphatic phosphoric acid mono- and/or di-ester containing from 1 to 4 carbon atoms

per alcoholic ester component, or up to 6 in the case of cycloaliphatic ester components, if desired in admixture with phosphoric acid,

0 and 20 weight % of isopropanol, and 0 and 20 weight % of citric acid, the balance being water, perfume and dye-

9. A method as claimed in claim 1, wherein the aqueous solution or suspension is substantially as described in any one of Examples 1 to 4 herein.

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